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(54) Title: **SONOELECTROCHEMICAL SYNTHESIS OF INORGANIC FULLERENE-LIKE NANOPARTICLES OF METAL CHALCOGENIDES**

(57) Abstract: Inorganic fullerene-like (IF) nanoparticles of metal chalcogenides, particularly molybdenum sulphide, including one or more layers of desired sizes and shapes, e.g., spheres, sphere-like, nanotubes and polyhedral shapes, are manufactured by sonoelectrochemical liquid-phase synthesis comprising: (a) dissolving in a suitable solvent: (i) at least one compound of said metal and at least one compound of said chalcogen, or (ii) at least one said chalcogen-containing said metal compound; (b) immersing an electrically conductive ultrasonic probe in the solution obtained in (a); (c) electrically connecting the ultrasonic probe, which operates as an electrode, to one terminal of an electric power supply, and the other terminal of said electric power supply is connected to a counter electrode; (d) applying an ultrasonic signal to said ultrasonic probe electrode and an electric voltage to both the ultrasonic probe electrode and the counter electrode; and (e) recovering the IF-metal chalcogenide structures that precipitated in step (d).

SONOELECTROCHEMICAL SYNTHESIS OF INORGANIC FULLERENE-LIKE NANOPARTICLES OF METAL CHALCOGENIDES

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FIELD AND BACKGROUND OF THE INVENTION

The present invention relates in general to a method for preparing inorganic fullerene-like structures of metal, e.g. transition metal, chalcogenides, particularly, to sonoelectrochemical synthesis of such inorganic fullerene-like structures, and
10 more particularly to room temperature sonoelectrochemical synthesis of molybdenum sulphide.

Since the discovery of the original fullerenes, C_{60} and C_{70} ^[1] and, retrospectively, multi-shell closed carbon structures ^[2], a wide range of related fullerene-like structures have been identified. These include closed structures of
15 other materials such as WS_2 ^[3], MoS_2 ^[4], $NiCl_2$ ^[5] and other shapes, in particular nanotubes, of many of the above materials ^[1,3,5,6] as well as of BN ^[7] and VO_x .^[8] All these closed structures require high temperatures for their formation to provide the high energy needed for their closure. Methods used to provide these temperatures include, besides the arc discharge technique commonly used for
20 carbon fullerenes ^[9], laser vaporization ^[1] and heating in a furnace.^[3,4] Other techniques, based on local heating, include electron ^[10] and ion beam ^[11] treatment and high electric current densities from an STM tip.^[12] Room temperature crystallization of amorphous WS_3 into closed structures of WS_2 has been reported to occur over several years ^[10], demonstrating the thermodynamic stability of these
25 structures, but illustrating the large kinetic barriers for their formation.

Particles of inorganic structures having a layered configuration (a single layer or nested layers) are known as inorganic fullerenes (IF). For ease of discussion, inorganic layered structures such as, but not limited to, spheres, whiskers, nanotubes, polyhedral and others, will interchangeably be referred to as
30 "inorganic fullerene-like" or "IF" materials, throughout the specification.

Nanoclusters of IF metal chalcogenide materials, such as WS₂ and MoS₂, were recently described (Refs. 3 and 10 herein and EP 0 580 019). Thus, according to European Patent No. 0 580 019 of the same applicants, a method was described for the preparation of oriented thin films of the transition metal chalcogenides WS₂, WSe₂, MoS₂ and MoSe₂ from the corresponding metal oxides, whereby in some conditions the nanoclusters of the layered IF metal chalcogenide materials were shown to be unstable against folding and to close upon themselves to form nested IF nanoparticles such as nested fullerene-like structures and nanotubes. These conditions could not be controlled and thus the method according to the above-mentioned publications do not allow to obtain high yields of macroscopic quantities of the IF metal chalcogenide, nor to determine the size and shape of the particles.

A gas phase synthesis for the preparation of a few milligrams of IF-MoS₂ from a molybdenum trioxide precursor and H₂S in a reducing atmosphere has been described, ^[4] taking advantage of the sublimation of the molybdenum suboxide (MoO_{3-x}) under reducing conditions above 700 °C. Thus, a portion of 30 mg of MoO₃ powder (>99% pure) was heated (>800 °C) and slowly reduced to MoO_{3-x} by a stream of forming gas (typically 5%H₂/95%N₂). The suboxide (MoO_{3-x}) sublimed and effused out of a nozzle where it crossed a stream of H₂S gas mixed with a forming gas. After some 3-5 minutes, the entire load (30 mg) of MoO₃ sublimed, the reaction products were collected on a quartz substrate, positioned few cm away from the crossing point of the two gas streams and maintained at the same temperature (>800 °C), and the collected nanoparticles were progressively converted into nested layer polyhedra within ca. 30 minutes of firing time. The average size of the oxide particles and the ensuing IF-MoS₂ particles increased with temperature. It was found that above 900 °C, platelets with 2H-MoS₂ structure abound, and became the sole product above 950 °C. According to the above-described gas phase reaction it is difficult to obtain very high quantities of

the IF structures of transition metal chalcogenides. The IF particles have several interesting and useful applications, and it would be very advantageous to have a method and apparatus for high yield preparation of macroscopic quantities of IF particles of metal, e.g. transition metal, chalcogenides.

5 The use of ultrasonic radiation to increase the rate of chemical reactions is well known and related to the phenomenon of cavitation, whereby very high local temperatures and pressures are transiently formed (sub- μ s) in collapsing bubbles.^[13] More recently, the combination of sonochemistry and electrochemistry (sonoelectrochemistry) has been investigated. Among the characteristics of this
10 technique are acceleration of mass transport, cleaning and degassing of the electrode surface and increased reaction rates.^[14] Sonoelectrochemical formation of nanoscale metal powders^[15] has been accomplished by applying an electric current pulse to nucleate the electrodeposit, followed by a burst of ultrasonic energy which removes the metal particles from the sonic probe cathode.

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SUMMARY OF THE INVENTION

Based on the assumption that the short bursts of local high temperature may allow formation of closed structures at nominal room temperature, we used the known process for cathodic electrodeposition of MoS₂ from solutions of
20 thiomolybdate ions.^[16,17] The MoS₂ deposited using this technique is normally amorphous as deposited and becomes crystalline after heat treatment forming a highly-textured film.^[17] This high degree of texture suggests a planar structure.

Using the same basic technique, but depositing onto an ultrasonic probe using the principle described above of a current pulse followed by an ultrasonic
25 pulse to remove the deposit from the probe/electrode, it was found that a black deposit of molybdenum sulphide formed in the solution.

It should be noted that the term "inorganic fullerene-like" ("IF"), as used herein in the specification and claims, refers to inorganic metal chalcogenide structures having one layer or nested layers which form what is known in the art as
30 a closed cage^[3] which may encage a void (i.e., be hollowed) or a core or may form

a stuffed nested layer structure, i.e. a structure containing a material other than the metal material precursor encaged within nested layers of the metal chalcogenide. In particular the term refers to structures such as what is known in the art as single and double layer inorganic fullerenes, nested layers inorganic fullerenes, stuffed
5 inorganic fullerenes, single layer nanotubes, nested nanotubes, stuffed nanotubes, and inorganic superlattice structures, i.e. IF particles having layers of two or more different chalcogenides of the metal, e.g. WS_2 and WSe_2 .

According to the method of the present invention, IF nanoparticles of metal chalcogenides including one or more layers of desired sizes and shapes, e.g.,
10 spheres, sphere-like, nanotubes and polyhedral shapes, may be manufactured.

The metals that are suitable for this method are metals that form layered metal chalcogenide products such as In, Ga, Sn and a transition metal selected from Mo, W, V, Zr, Hf, Pt, Re, Nb, Ta, Ti, Cr and Ru.

The present invention thus relates to a method for the sonoelectrochemical
15 liquid phase synthesis of inorganic fullerene-like (hereinafter IF) structures of metal chalcogenides, wherein said metal is selected from In, Ga, Sn and a transition metal selected from Mo, W, V, Zr, Hf, Pt, Re, Nb, Ta, Ti, Cr and Ru, and the chalcogen is S, Se or Te, the method comprising the steps of:

(a) dissolving in a suitable solvent: (i) at least one compound of said
20 metal and at least one compound of said chalcogen, or (ii) at least one said chalcogen-containing said metal compound;

(b) immersing an electrically conductive ultrasonic probe in the solution obtained in (a);

(c) electrically connecting the ultrasonic probe, which operates as an
25 electrode, to one terminal of an electric power supply, and the other terminal of said electric power supply is connected to a counter electrode;

(d) applying an ultrasonic signal to said ultrasonic probe electrode and an electric voltage to both the ultrasonic probe electrode and the counter electrode:
and

(e) recovering the IF metal chalcogenide structures that precipitated in step (d).

The solvent in step (a) may be aqueous or non-aqueous. Examples of non-aqueous solvents are, but not limited to, alcohols and dimethyl sulfoxide (DMSO). The synthesis is carried out at a temperature in which said solvent is in the liquid state. For example, when the solvent is water, the synthesis may be carried out at room temperature.

The ultrasonic probe is preferably a Ti probe. In a preferred embodiment, in step (d), first an electric voltage is applied to both the ultrasonic probe electrode and the counter electrode and is then followed by an ultrasonic signal to the ultrasonic probe electrode, and the sequences of electric voltage and ultrasonic signal are repeated until the desired amount of IF-metal chalcogenide structures is obtained.

In another preferred embodiment, the ultrasonic probe electrode is connected to the negative terminal of the electric power supply and the counter electrode is connected to the positive terminal.

As described above, the metals that are suitable for this method are metals that form layered metal chalcogenide products. Examples of metal chalcogenides that form layered products and are suitable for the preparation of IF structures according to the method of the invention include, but are not limited to, WS_2 , WSe_2 , MoS_2 , $MoSe_2$, SnS_2 , $SnSe_2$, RuS_2 , GaS , $GaSe$, In_2S_3 , In_2Se_3 , InS , $InSe$, etc. [for additional examples, see A. F. Wells, Structural Inorganic Chemistry, 5th edition, Oxford Science Publications (1993); Chemistry of the Elements, by N. N. Greenwood and A. Earnshaw, Pergamon Pres, Oxford (1990)].

The metal compound according to the invention may be an oxide that is soluble in an electrolyte, for example MoO_3 and WO_3 , that are soluble in alkaline solutions.

The chalcogen according to the invention is S, Se or Te, and the chalcogen compound may be a chalcogen, a compound containing a chalcogen, a mixture of chalcogens, a mixture of compounds containing a chalcogen and a mixture of a

chalcogen and a compound containing a chalcogen. The chalcogen material is preferably a chalcogen compound such as H_2S , H_2Se , and/or H_2Te , Na_2S , Na_2Se , and/or Na_2Te , and CS_2 .

The size of the IF particles produced by the method of the invention is in the
5 nanometer range, typically some tens of nanometers and also hundreds of nanometers. Nanotubes may be even longer.

The IF structures produced by the method of the invention include, but are not limited to, single layer inorganic fullerenes, nested layers inorganic fullerenes, stuffed inorganic fullerenes, single layer nanotubes, nested nanotubes, stuffed
10 nanotubes, inorganic supperlattice structures, and structures with negative curvature (Schwartzites).

In a preferred embodiment, the metal is a transition metal selected from Mo, W, V, Zr, Hf, Pt, Re, Nb, Ta, Ti, Cr and Ru, more preferably it is Mo.

In a preferred embodiment, the invention relates to a method for the
15 sonoelectrochemical synthesis of inorganic fullerene-like (hereinafter IF) structures of molybdenum sulphide, comprising the steps of:

- (a) dissolving in a suitable solvent at least one molybdenum compound and at least one sulphur compound or a sulphur-containing molybdenum compound;
- 20 (b) immersing an electrically conductive ultrasonic probe in the solution obtained in (a);
- (c) electrically connecting the ultrasonic probe, which operates as an electrode, to one terminal of an electric power supply, and the other terminal of said electric power supply is connected to a counter electrode;
- 25 (d) applying an ultrasonic signal to said ultrasonic probe electrode and an electric voltage to both the ultrasonic probe electrode and the counter electrode: and
- (e) recovering the molybdenum sulphide IF structures that precipitated in step (d).

In a most preferred embodiment, the method for sonoelectrochemical liquid phase synthesis of IF-like structures of molybdenum sulphide is carried out at room temperature, comprising the steps of:

- (a) dissolving ammonium tetrathiomolybdate in water;
- 5 (b) immersing an electrically conductive ultrasonic Ti probe in the solution obtained in (a);
- (c) electrically connecting the ultrasonic probe, which operates as an electrode, to one terminal of an electric power supply, and the other terminal of said electric power supply is connected to a counter electrode;
- 10 (d) applying an ultrasonic signal to said ultrasonic probe electrode and an electric voltage to both the ultrasonic probe electrode and the counter electrode, and repeating sequentially the pulses of electric voltage and ultrasonic signal until the desired amount of molybdenum sulphide IF structures is deposited; and
- (e) recovering the thus precipitated molybdenum sulphide IF structures.

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BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1. Transmission electron microscopy (TEM) image of the sonoelectrochemically-prepared MoS_2 powder. The inset in the top lefthand corner shows part of the image at x 2 magnification.

20 Fig. 2. TEM images of the same MoS_2 particle taken with the sample rotated in the direction of the electron beam at an angle of A +45°; B 0°; C -45°.

Fig. 3. TEM image of part of a MoS_2 nanotube.

Fig. 4. TEM image of a large MoS_2 polyhedral structure filled with MoO_2 . The inset at the top lefthand corner shows part of the image at x 3 magnification.

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DETAILED DESCRIPTION OF THE INVENTION

The invention will be illustrated by the following non-limiting examples and their figures.

Experimental: We used a sonoelectrochemical device similar to the one
30 described by Reisse and co-workers.^[15] A titanium horn (liquid processor, 20 kHz)

acts as both the cathode and the ultrasound emitter. The electroactive part of the sonoelectrode is the planar circular surface at the bottom of the horn. A constant current deposition pulse (160 mAcm^{-2}) was immediately followed by a sonic pulse (16 W intensity). The on and off times of both current and sonic pulses were the same (0.34 s). A spiral made of platinum wire (0.5 mm diameter and 15 cm long) was used as counter electrode, and the intensity - 16 W. The electrolyte (100 ml) was an aqueous solution of 50 mM ammonium tetrathiomolybdate $[(\text{NH}_4)_2\text{MoS}_4]$ and 1 M sodium sulfate $[\text{NaSO}_4]$ at a pH of 6.0. The deposition was continued for ca. 90 minutes. At the end of the reaction, the precipitate was centrifuged, washed repeatedly with acetone and dried under vacuum.

A transmission electron microscopy (TEM) image of a sample of this powder is shown in Fig. 1. Although there is considerable variation in the size and shape of the individual particles, they are typically several tens of nm in size and most of the particles have sizes which are the same order of magnitude in all three dimensions. However, there is some variability in the shapes, as can be seen in Fig. 1, where the dimension can be twice as much in one direction as in the others. The crystalline layers (typically between 12 and 15) of MoS_2 can be clearly seen surrounding a featureless core. From such a two-dimensional picture, we cannot tell if the particles are in the form of discs (or cylinders) or whether they are surrounded by the MoS_2 layers in all directions like the $\text{W}(\text{Mo})\text{S}_2$ fullerene-like structures.

Fig. 2 displays TEM images of the same particle at different orientations to the electron beam. The fact that the molecular layers are seen at different angles is a convincing demonstration of the curved and closed nature of the structures. If the sample were flat, as is normally the case for this material, an image of the layers would be seen only when the layers were aligned with the electron beam. In a closed, curved structure, part of the layers will always be aligned with the beam, regardless of the orientation. By the same argument, the different (002) planes will only be visible when they are approximately parallel to the electron beam, i.e., at the outer portions of the 'spheres'. They will become increasingly less visible

toward the center of the structure. Also, if we assume a roughly spherical shape, the particle will be thicker near the center, resulting in less transmission of the electron beam and loss of information. Therefore we cannot state definitively if these structures are made up entirely of MoS₂ sheets, are hollow or contain a core of another material (MoO₂, amorphous MoS₂). The presence of MoS₂ planes inside the closed structures, but oriented in various directions, as seen in Fig. 2 (and particularly clearly in Fig. 2(c)) suggests that the structures are hollow to some extent. Some of these planes could lie on the outer surface of the structures; however the observation that they almost always terminate within the boundaries of the closed structures suggest that this is less likely.

Occasionally seen, are nanotubes, with the long axis much larger than the cross section (Fig. 3 shows part of one of these nanotubes). Also sometimes seen are larger (>100 nm), irregularly-shaped polyhedral structures (Fig. 4). The number of MoS₂ layers in these larger structures is no greater than in the smaller ones and most of the structure is featureless to TEM. However, ED of the structure in Fig. 4 showed the presence of MoO₂ in addition to MoS₂. X-ray diffraction (not shown) confirmed the presence of MoO₂ (monoclinic, powder pattern 32-671). In addition the (002) reflection of the MoS₂ was shifted slightly to lower angles. The shift to smaller angles compared with normal MoS₂ can be explained either by strain-induced lattice expansion characteristic of closed Mo(W)S₂ structures^[4,18] or to the presence of oxygen as MoO_xS₂.^[19]

Recently, the sonochemical synthesis of MoS₂ has been reported by Mdleleni et al..^[20] In this work, Mo(CO)₆ and elemental sulphur in tetramethylbenzene were subjected to high intensity ultrasonic radiation. The initially formed MoS₂, which was amorphous, was crystallized by heating at 450°C for 10 hr to give a layered, nanostructured product. In order to check if our MoS₂ could also be formed in the absence of an electrochemical process, our electrodeposition solution was subjected to ultrasonic radiation (16 W continuous radiation for 90 mn). A brown-black powder was formed in the solution. This powder was completely diffraction amorphous (no XRD or electron diffraction pattern could be discerned, even at a

very slow XRD scan rate of 0.15°/mn). On heating to 400°C, a mixture of MoS₂ and various phases of MoO₃ were found by XRD. Therefore, the combination of both electrochemical and ultrasonic processes was necessary to form the crystallized and closed MoS₂ structures from the solution used by us. We note that Mdlelini et al.
5 obtained curved nanostructures in their annealed samples (seen from the TEM micrograph in fig. 2 of their paper). It is possible that their structures are also closed - either partially or completely; however, in the absence of angle-dependent micrographs, this cannot be determined from their paper.

We suggest the following mechanism to explain formation of the closed
10 curved structures. Amorphous MoS₂ is formed by electrodeposition onto the sonic probe cathode. The subsequent sonic shock wave then removes this deposit from the probe surface. The deposit could be spheroidal (nucleating electrodeposits are often nanoparticulate) or planar (crystalline MoS₂ would probably form as sheets, but the amorphous material is less likely to do so). At this point, it is conceivable
15 that the effect of this shock wave is itself sufficient to crystallize the deposit. More probable, however, is that the cause of the crystallization, and possibly bending, which normally require high temperatures, is the collapse of the cavitation bubbles.

Electrodeposition or ultrasonic irradiation alone result in X-ray amorphous Mo-S products, but the combination of both gives well-crystallized closed
20 structures of MoS₂. This technique allows room temperature preparation of large amounts of closed MoS₂ nanoclusters. Ultrasonic radiation is as useful for inducing physical reactions (in this case, crystallization and shaping) as it is for chemical reactions. The combination of electrochemical and sonic processes provide many experimental variables which allow control of particle size, shape, and size and
25 shape distribution and will probably be applicable to the formation of closed structures of other layered compounds which can be prepared by electrochemical (and quite likely also chemical) techniques.

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CLAIMS:

1. A method for the sonoelectrochemical liquid-phase synthesis of inorganic fullerene-like (hereinafter IF) structures of metal chalcogenides, wherein said metal
5 is selected from In, Ga, Sn and a transition metal selected from Mo, W, V, Zr, Hf, Pt, Re, Nb, Ta, Ti, Cr and Ru., and the chalcogen is S, Se or Te, the method comprising the steps of:
 - (a) dissolving in a suitable solvent: (i) at least one compound of said metal and at least one compound of said chalcogen, or (ii) at least one said
10 chalcogen-containing said metal compound;
 - (b) immersing an electrically conductive ultrasonic probe in the solution obtained in (a);
 - (c) electrically connecting the ultrasonic probe, which operates as an electrode, to one terminal of an electric power supply, and the other terminal of
15 said electric power supply is connected to a counter electrode;
 - (d) applying an ultrasonic signal to said ultrasonic probe electrode and an electric voltage to both the ultrasonic probe electrode and the counter electrode:
and
 - (e) recovering the IF-metal chalcogenide structures that precipitated in step (d).
20
2. The method according to claim 1 wherein said suitable solvent in step (a) is aqueous or non-aqueous.
3. The method according to claim 1 or 2, wherein the synthesis is carried out at
25 a temperature in which said solvent is in the liquid state.
4. The method according to claim 3, wherein said solvent is water and the synthesis is carried out at room temperature.

5. The method according to any one of claims 1 to 4, wherein said ultrasonic probe is Ti.
6. The method according to any one of claims 1 to 5, which comprises
5 applying in step (d) first an electric voltage to both the ultrasonic probe electrode and the counter electrode which is then followed by an ultrasonic signal to the ultrasonic probe electrode, and repeating the sequences of electric voltage and ultrasonic signal until the desired amount of IF-metal chalcogenide structures is obtained.
- 10 7. The method according to claim 6, wherein the ultrasonic probe electrode is connected to the negative terminal of the electric power supply and the counter electrode to the positive terminal.
- 15 8. The method according to any one of claims 1 to 7, wherein the metal is a transition metal selected from Mo, W, V, Zr, Hf, Pt, Re, Nb, Ta, Ti, Cr and Ru.
9. The method according to claim 8, wherein said metal is Mo.
- 20 10. A method for the sonoelectrochemical liquid phase synthesis of inorganic fullerene-like (hereinafter IF) structures of molybdenum sulphide, comprising the steps of:
- (a) dissolving in a suitable solvent: (i) at least one molybdenum compound with at least one sulphur compound, or (ii) a sulphur-containing
25 molybdenum compound;
- (b) immersing an electrically conductive ultrasonic probe in the solution obtained in (a);
- (c) electrically connecting the ultrasonic probe, which operates as an electrode, to one terminal of an electric power supply, and the other terminal of
30 said electric power supply is connected to a counter electrode;

(d) applying an ultrasonic signal to said ultrasonic probe electrode and an electric voltage to both the ultrasonic probe electrode and the counter electrode; and

5 (e) recovering the molybdenum sulphide IF structures that precipitated in step (d).

11. A method according to claim 10 for room temperature sonoelectrochemical synthesis of inorganic fullerene-like (hereinafter IF) structures of molybdenum sulphide, comprising the steps of:

10 (a) dissolving ammonium tetrathiomolybdate in water;

(b) immersing an electrically conductive ultrasonic Ti probe in the solution obtained in (a);

(c) electrically connecting the ultrasonic probe, which operates as an electrode, to one terminal of an electric power supply, and the other terminal of
15 said electric power supply is connected to a counter electrode;

(d) applying an ultrasonic signal to said ultrasonic probe electrode and an electric voltage to both the ultrasonic probe electrode and the counter electrode, and repeating sequentially the pulses of electric voltage and ultrasonic signal until the desired amount of molybdenum sulphide IF structures is deposited; and

20 (e) recovering the thus precipitated molybdenum sulphide IF structures.



Fig. 1

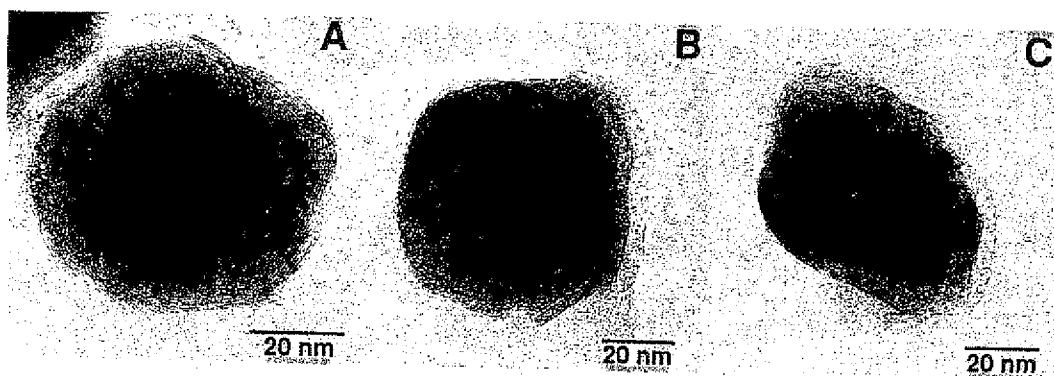


Fig. 2A

Fig. 2B

Fig. 2C



Fig. 3

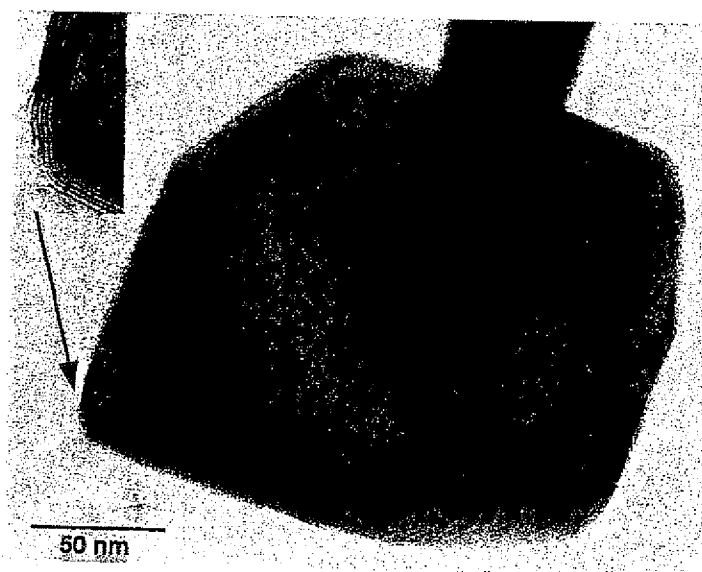


Fig. 4

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/IL 00/00408

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C25B1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal, WPI Data, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 33871 A (UNIVERSITE LIBRE DE BRUXELLES) 14 December 1995 (1995-12-14) page 17 -page 19; claims 1-14	1
A	J. REISSE: "Quantitative sonochemistry" ULTRASONICS SONOCHEMISTRY, no. 3, 1996, pages 147-151, XP002153735 page 149, paragraph 4 -page 150 page 150; example 9; table 2	1
A	DE 38 26 281 A (HAHN-MEITNER-INSTITUT BERLIN GMBH) 1 February 1990 (1990-02-01) column 3 -column 4; claims 1-11	1,10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

23 November 2000

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. Appl. No.

PCT/IL 00/00408

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9533871 A	14-12-1995	BE 1008304 A AU 2558595 A	02-04-1996 04-01-1996
DE 3826281 A	01-02-1990	NONE	